

A first-principles study of the electronic structure and stability of $\text{Be}(\text{BH}_4)_2$

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(Dated: February 2, 2008)

Alanates and boranates are studied intensively because of their potential use as hydrogen storage materials. In this paper we present a first-principles study of the electronic structure and the energetics of beryllium boranate, $\text{Be}(\text{BH}_4)_2$. From total energy calculations we show that - in contrast to the other boranates and alanates - hydrogen desorption directly to the elements is likely, and is at least competitive with desorption to the elemental hydride (BeH_2). The formation enthalpy of $\text{Be}(\text{BH}_4)_2$ is only -0.12 eV/ H_2 (at $T = 0\text{K}$). This low value can be rationalized by the participation of all atoms in the covalent bonding, in contrast to the ionic bonding observed in other boranates. From calculations of thermodynamic properties at finite temperature we estimate a decomposition temperature of 162 K at a pressure of 1 bar.

PACS numbers: 61.50.Lt, 65.40.-b, 71.20.Nr

Keywords:

I. INTRODUCTION

In the last decade the environmental importance of reducing the CO_2 exhaust has been widely accepted. The use of hydrogen based fuel cells is an important contribution to achieve this reduction. One major obstacle for this use is the development of a method for hydrogen storage with a high gravimetric and volumetric hydrogen density.¹

One way of storing hydrogen is in a (complex) metal hydride. The ideal hydrogen storage material should have the highest possible gravimetric hydrogen density. This obviously requires the use of lightweight materials. Moreover, the formation energy of the hydride has to be such that it is stable at atmospheric conditions, yet it has to decompose at a moderate temperature to release the hydrogen. A further important point is that the reactions involved in hydrogen de/absorption must have fast kinetics.

Over the last decade alanates and boranates have been studied extensively as potential hydrogen storage materials.^{1,2} Alanates and boranates consist of a lattice of metal cations and $(\text{AlH}_4)^-$ or $(\text{BH}_4)^-$ complex anions, respectively. Generally these materials decompose by heating via intermediate complex hydrides into bulk metals, elemental hydrides and hydrogen gas. In the last few years the attention has gradually shifted from alanates towards boranates, because of the high gravimetric hydrogen density in the latter. Many boranates turn out to be too stable, however.

In principle a large variety of boranates can be synthesized by changing the metal cations, which can be used to tune the formation energy.³ So far most effort has been devoted to the alkali boranates,^{4,5,6,7,8,9,10} and more recently to mixtures of alkali boranates,^{11,12} and to the alkaline earth boranates.^{13,14,15,16,17} In order to

understand the chemical trends we have recently developed a simple model for the formation energies of these compounds.¹⁸ This model demonstrates that these boranates are ionic compounds (in the sense discussed above) and that the difference in their formation energies can be understood on the basis of the electrostatic (Madelung) lattice energy. The basic stability of the $(\text{BH}_4)^-$ cation is not affected by substituting one alkali or alkaline earth cation by another.

The stability of $(\text{BH}_4)^-$ may be changed by adding an element that competes with boron in binding with hydrogen. To investigate this possibility we study beryllium boranate, $\text{Be}(\text{BH}_4)_2$,¹⁹ in this paper. Establishing the electronic structure and thermodynamic stability of $\text{Be}(\text{BH}_4)_2$ will assist in understanding the chemical and physical trends in alkali, alkaline earth alanates and boranates.²⁰

We present a first principles study of the electronic structure and the thermodynamic properties of $\text{Be}(\text{BH}_4)_2$. The electronic structure in relation to the crystal structure is used to analyze the bonding in $\text{Be}(\text{BH}_4)_2$. We calculate total energies and phonon frequencies of all compounds involved in possible formation reactions of $\text{Be}(\text{BH}_4)_2$. From these data we obtain the thermodynamic properties at finite temperature.

II. COMPUTATIONAL METHODS

First-principles calculations are carried out within the density functional theory (DFT) approach, applying a generalized gradient approximation (GGA) for the exchange correlation functional.²¹ We use a plane wave basis set and the projector augmented wave (PAW) method,^{22,23} as implemented in the Vienna *Ab initio* Simulation Package (VASP),^{24,25,26} and apply non-linear

core corrections.²⁷

Brillouin zone integrations are performed with a tetrahedron method²⁸ for calculating total energies. A Gaussian smearing method is used for calculating densities of states, with a smearing parameter of 0.1 eV. The \mathbf{k} -point meshes are such that total energies are converged within 0.1 meV per formula unit. The total energies used in the calculations of the reaction enthalpies are calculated with a high plane wave kinetic energy cutoff of 700 eV. By varying the computational parameters, in particular by trying different PAW potentials,²⁹ we estimate that reaction enthalpies are converged on a scale of 5 meV.

The atomic positions and lattice parameters are relaxed using a conjugate gradient algorithm for a range of fixed volumes. The total energy versus volume curve obtained this way is fitted with a Murnaghan's equation of state expression, which yields the ground state volume, the bulk modulus, and its pressure derivative.³⁰ At the ground state volume we relaxed the atomic positions and lattice parameters to obtain the ground state structure. This procedure is followed for all compounds mentioned in this paper.

To calculate the zero point energies (ZPE) and phonon densities of state we need the phonon frequencies of all these compounds. Vibrational frequencies are obtained from the dynamical matrix, whose matrix elements (the force constants) are calculated using a finite difference method.³¹ The force constants are calculated from displacements of 0.005 Å in two opposite directions for each atomic degree of freedom. For both bulk beryllium and beryllium hydride $2 \times 2 \times 2$ supercells give converged ZPEs. One does not need a supercell to calculate the phonon frequencies of $\text{Be}(\text{BH}_4)_2$, since the unit cell of $\text{Be}(\text{BH}_4)_2$ is sufficiently large. For boron we use the frequencies that have been reported earlier.³²

III. CRYSTAL STRUCTURE

$\text{Be}(\text{BH}_4)_2$ can be synthesized by the reaction of lithium boranate and beryllium chloride.^{33,34} Its crystal structure consists of helical polymers of alternating beryllium and boron atoms (B_b) that are connected via pairs of hydrogen atoms (H_b).³⁵ The polymer building block is shown schematically in Fig. 1. A further boron atom (B_d) is attached to each beryllium atom, again via a pair of hydrogen atoms (H_c) and this B_d atom also binds two “dangling” hydrogen atoms (H_d). The polymers are packed in the crystal structure as shown in Figure 2. On the basis of this structure one may expect a strong bonding between the atoms in one polymer chain, and a much weaker bonding between the polymer chains. The latter is reflected in the low melting point of $\text{Be}(\text{BH}_4)_2$ of 125°C.

We relaxed the crystal structure of $\text{Be}(\text{BH}_4)_2$ as described in the previous section, including the cell volume, lattice parameters and atomic positions, while keeping the experimental space-group and Wyckoff positions.

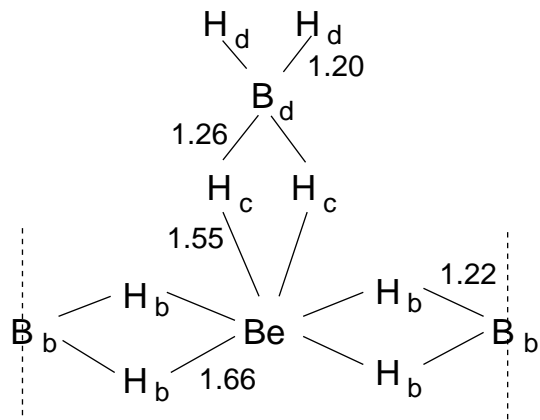


FIG. 1: Schematic bonding scheme and labeling of the atoms within a polymer chain in $\text{Be}(\text{BH}_4)_2$. The three dimensional structure is given in Fig. 2. The numbers indicate optimized bond lengths in Å.

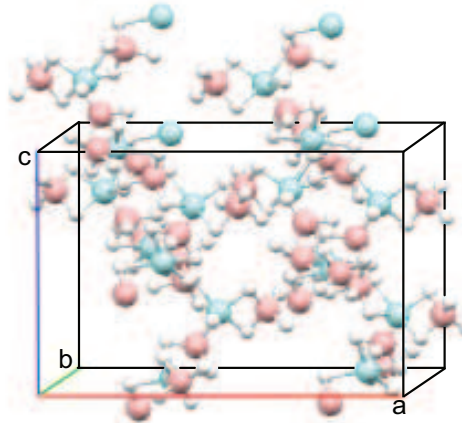


FIG. 2: (Color online) Crystal structure of $\text{Be}(\text{BH}_4)_2$.

Except for the cell volume, the parameters compare well to the experimental values.³⁵ The calculated cell volume is 15% larger than the experimental cell. This indicates that the binding between the polymer chains is indeed weak and of van der Waals type. It is well-known that, using the common functionals, DFT fails to capture van der Waals bonding. However, the total energy difference between the experimental and calculated cell volumes is less than 5 meV/ H_2 . This error only has a minor effect on the relative total energies.

The optimized B–H and Be–H bond lengths are given in Fig. 1. As references, the B–H bond length in a $(\text{BH}_4)^-$ anion is 1.21 Å, whereas a B–H bond length in a typical three center B–H–B bond is 1.34 Å.³³ Comparison with these numbers indicates that the B–H bonding in $\text{Be}(\text{BH}_4)_2$ is closer to that in the $(\text{BH}_4)^-$, although there is some distortion due to the presence of the Be atom, in particular on the B_d – H_c bond. This could indicate some competition between B and Be for bonding

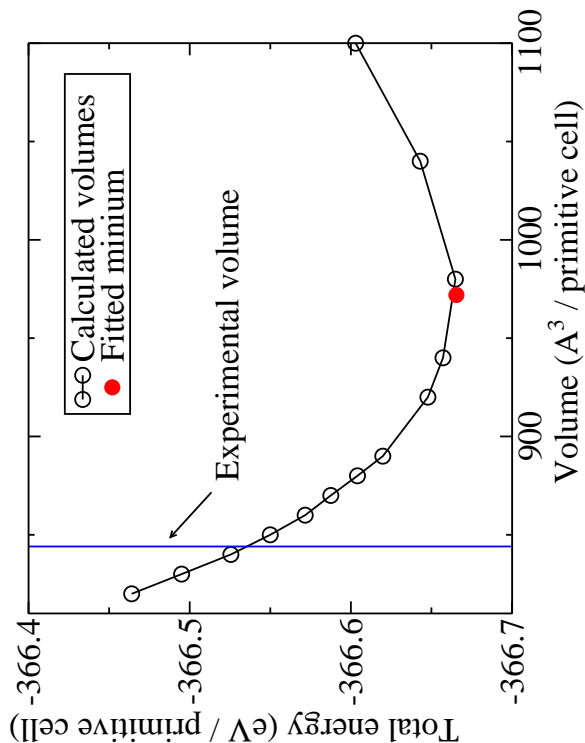


FIG. 3: Total energy per unit cell of $\text{Be}(\text{BH}_4)_2$ as a function of the cell volume.

TABLE I: Optimized atomic positions of $\text{Be}(\text{BH}_4)_2$. The space group is $I4_1cd$ (110) and all atoms are on Wyckoff positions 16b. The optimized lattice parameters are $a, b, c = 14.28, 14.28, 9.54$ Å.

atom	x	y	z
Be	0.2050	0.0992	0.0016
B _d	0.1695	0.9702	0.0068
B _b	0.1503	0.1978	0.1237
H _d	0.0997	0.9439	0.0653
H _d	0.2183	0.9130	0.9499
H _c	0.2189	0.0123	0.0963
H _c	0.1453	0.0294	0.9157
H _b	0.1083	0.1649	0.0231
H _b	0.2281	0.1647	0.1450
H _b	0.1611	0.2813	0.1003
H _b	0.1027	0.1793	0.2269

to hydrogen. For comparison, the B–H bond lengths in alkali boranates are all very close to 1.21 Å. The Be–H bond lengths are still quite large, however, which indicates a significant ionic contribution to the bonding.

We have also optimized the structure of BeH_2 , see Table II. It agrees well with the experimental structure³⁶ and with that obtained in a previous calculation,³⁷ the largest difference being that our calculated bulk modulus (21.4 GPa) is ~ 10 % smaller than that calculated in Ref. 37 (23.8 GPa). For elemental boron we use the β -

TABLE II: Optimized crystal structure of BeH_2 . The space group is $Ibam$ (72) and the optimized lattice parameters are $a, b, c = 8.967, 4.141, 7.643$ Å. The experimental lattice parameters are $a, b, c = 9.082, 4.160, 7.707$ Å.³⁶

atom	Wyckoff	x	y	z
Be	4a	0	0	0.25
Be	8j	0.1677	0.1200	0
H	16k	0.0882	0.2241	0.1520
H	8j	0.3102	0.2771	0

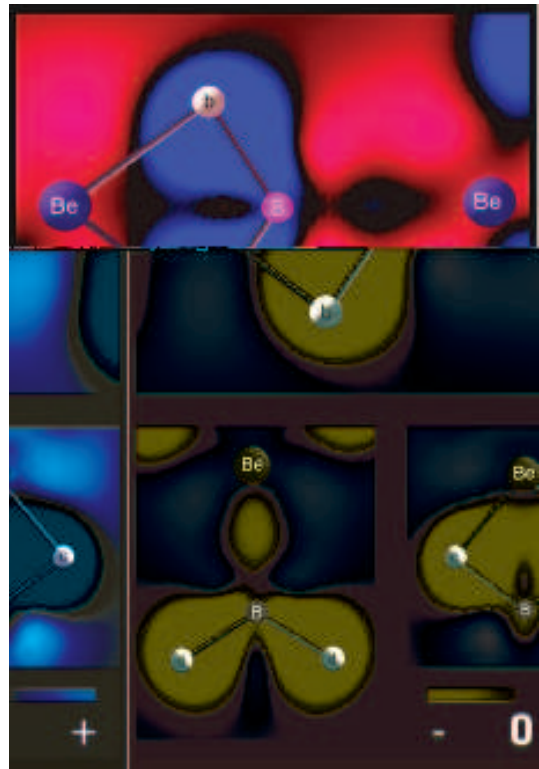


FIG. 4: (color online) Charge density difference plots of $\text{Be}(\text{BH}_4)_2$ with respect to the isolated atoms. The top picture gives a cut through a plane containing B_b, H_b and Be atoms of the polymer backbone, the bottom left picture a cut through the B_d, H_c side chain plane, and the bottom right picture a cut through the B_d, H_d side chain plane.

orthorhombic structure as given in Ref. 32. For elemental beryllium (space group $P\bar{3}m1$ (164)) we find lattice parameters $a = 2.260$ Å and $c = 3.567$ Å, which compare well to the experimental values of 2.29 Å and 3.60 Å, respectively.³⁸

IV. ELECTRONIC STRUCTURE

As discussed above the crystal structure of $\text{Be}(\text{BH}_4)_2$ indicates a weak bonding between polymer chains, and a stronger bonding within a polymer chain. The charge displacement upon bond formation can be visualized by

plotting the charge density difference, i.e. the charge density of $\text{Be}(\text{BH}_4)_2$ minus that of the individual isolated atoms. Cuts through the charge density difference in various planes along a polymer backbone are shown in Fig. 4. They clearly indicate the formation of B–H covalent bonds, which are polarized somewhat towards the H atoms. The character of the Be–H bonds is much less clear from these plots. In any case these bonds are strongly polarized in the direction of the H atoms.

The electronic projected density of states (PDOS) of $\text{Be}(\text{BH}_4)_2$, projected on s, p components of the individual atoms, is shown in Fig. 5. Tetrahedrally bonded BH_4^- generates a characteristic pattern in the valence band part of the PDOS, which is qualitatively similar to that observed for AlH_4^- tetrahedra in the aluminates.^{39,40,41,42,43,44} The tetrahedral geometry of BH_4^- results in a splitting into two valence peaks, the lower one of s (A_1) symmetry and the upper one of p (T_2) symmetry, with a relative weight ratio of 1:3. Projected on atomic states, the s -peak then has contributions from H s and B s orbitals, and the p -peak has contributions from H s and B p orbitals. The p -peak can be split due to symmetry breaking caused by the crystal field. This is clearly observed in the lowest two panels of Fig. 5, showing the PDOS on the B_d and H_d atoms with the s peak at ~ -7 eV, and a p doublet around ~ -1 eV. The splitting between s - and p -peaks is large (~ 6 eV), and the crystal field splitting is much smaller (~ 1 eV).

The interaction between the BH_4 units in the crystal lattice leads to a broadening of the peaks due to band formation. The interaction is strongest along the $\text{B}_b(\text{H}_b)_4\text{-Be-B}_b(\text{H}_b)_4$ polymer backbone, see Figs. 1 and 2. This leads to an s -type band in the range ~ -9 to ~ 7.5 eV, involving contributions from H_b , B_b , and Be s orbitals, whose DOS has the characteristic shape of a one-dimensional structure, see the upper three panels of Fig. 5. In the range ~ -5 to ~ -2 eV we find a set of p -type bands. The band widths are smaller than the sp splitting, but they are not negligible, reflecting the covalent bonding along the polymer backbone.

The involvement of the Be atoms can be clarified by calculating the DOS for a $\text{Be}(\text{BH}_4)_2$ structure in which the Be atoms are replaced by a homogeneous background with charge 2+. The result is shown in Fig 6. The s and p valence bands discussed above disappear and are replaced by much narrower peaks that reflect electron localization on BH_4^- ions in this artificial structure. In other words, the Be atoms in $\text{Be}(\text{BH}_4)_2$ are involved in the covalent bonding. This is in contrast to alkali or alkaline earth borates and aluminates, where the DOS changes little if the cations are replaced by a background charge. The bonding in the latter compounds can be described as an ionic bonding between BH_4^- or AlH_4^- anions and M^+ (alkali) or M^{2+} (alkaline earth) cations.⁴⁴

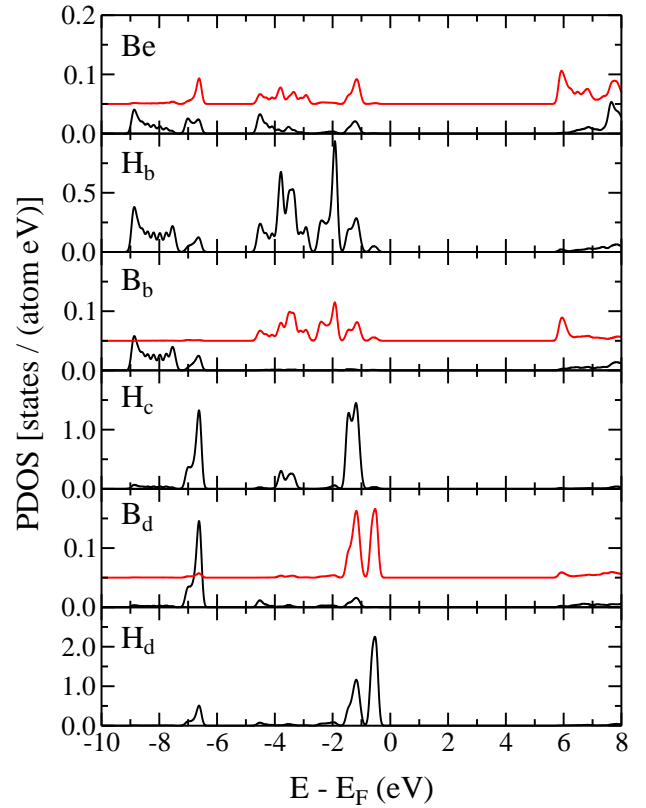


FIG. 5: (color online) The electronic projected densities of states (PDOS) of $\text{Be}(\text{BH}_4)_2$. The Fermi level, E_F , at the top of the valence band is the zero of energy. The upper (red) and lower curves (black) give projections on p and s atomic states, respectively. Atomic radii of 0.7, 0.5 and 1.1 Å are used for Be, B and H.

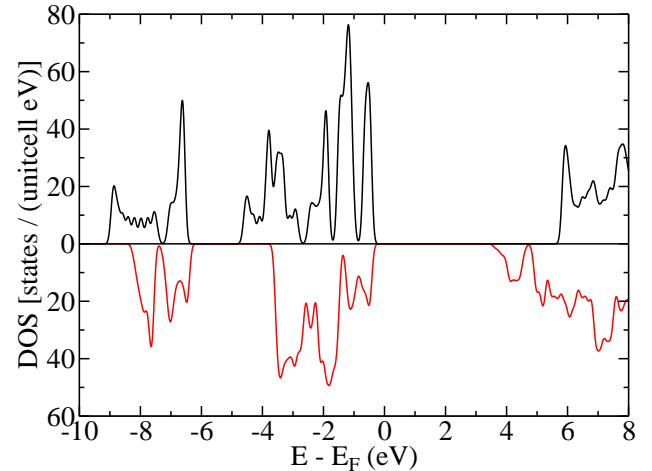


FIG. 6: (color online) The total electronic densities of states (DOS) of $\text{Be}(\text{BH}_4)_2$. The Fermi level, E_F , at the top of the valence band is the zero of energy. In the lower curve the beryllium atoms are replaced by an homogeneous background with charge 2+.

V. REACTION ENTHALPIES

For light elements such as hydrogen, beryllium and boron the quantum character of their atomic vibrations is important. This leads to vibrational energies at zero temperature that are not negligible. For each compound involved in the reaction we calculate its zero point vibrational energy (ZPVE) from the frequencies of the vibrational modes in the optimized structure. For hydrogen molecules also the zero point rotational energy (ZPRE) is not entirely negligible. Reaction enthalpies ΔH at $T = 0\text{K}$ are then calculated from

$$\Delta H = \sum_p (E_p^{\text{tot}} + E_p^{\text{ZPVE}}) + E_{\text{H}_2}^{\text{ZPRE}} - \sum_r (E_r^{\text{tot}} + E_r^{\text{ZPVE}}) \quad (1)$$

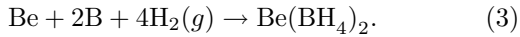
where $E_{p/r}^{\text{tot}}$ denotes the total energy of the reaction products p or reactants r , $E_{p/r}^{\text{ZPVE}}$ are the corresponding ZPVEs, and $E_{\text{H}_2}^{\text{ZPRE}}$ is the ZPRE of the hydrogen molecules involved in the reaction.

For the hydrogen molecules we calculate a vibrational frequency of 4356 cm^{-1} , in good agreement with the experimental value of 4401 cm^{-1} .⁴⁵ The ZPVE, 0.266 eV , is then calculated from the energy levels of a Morse potential,

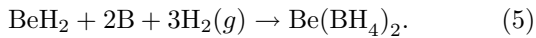
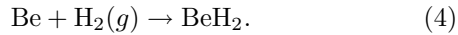
$$E(n) = \hbar\omega \left(n + \frac{1}{2} \right) - \frac{1}{4D_e} \left[\hbar\omega \left(n + \frac{1}{2} \right) \right]^2, \quad (2)$$

where ω is the vibration eigenfrequency and $D_e = 4.57\text{ eV}$ is the dissociation energy. Assuming that ortho- and para-hydrogen are produced in a proportion of three to one, the average ZPRE of a hydrogen molecule is 0.011 eV , using the energy levels given in Ref. 45.

The calculated total energies and ZPEs of all compounds involved in the reactions are listed in Table III. We consider two possible reaction paths for the formation of $\text{Be}(\text{BH}_4)_2$. In the first path $\text{Be}(\text{BH}_4)_2$ is directly formed from the elements.



The second path involves the formation of an intermediate compound BeH_2 .



The enthalpies of these reaction are calculated using Eq. (1) and the values given in Table III.

Equation (3) gives a reaction enthalpy of -0.39 eV/H_2 if ZPEs are neglected. If ZPEs are included the reaction enthalpy becomes -0.12 eV/H_2 , which indicated the importance of ZPE corrections for these lightweight compounds. In principle these values are in a range that is useful for hydrogen storage. Using the ionic model of Ref.¹⁸ gives a reaction enthalpy of -0.02 eV/H_2 (neglecting ZPEs). In the previous section we have already

TABLE III: Total energies (with respect to non spin polarized model atoms), zero point vibrational energies (ZPVE) and zero point rotational energy (ZPRE) in eV/formula unit in the relaxed structures.

	E^{TOT}	E^{ZPVE}	E^{ZPRE}
$\text{Be}(\text{BH}_4)_2$	-43.353	2.450	
BeH_2	-10.797	0.542	
H_2	-6.803	0.266	0.011
B	-6.687	0.126	
Be	-3.729	0.091	

concluded that the bonding in $\text{Be}(\text{BH}_4)_2$ is not purely ionic, i.e. $\text{Be}^{2+}(\text{BH}_4)_2^-$. The Be atoms are bonded (partially) covalently to BH_4 , which increases the bonding as compared to the pure ionic picture, resulting in a higher dehydrogenation enthalpy.

Most aluminates and other boranates form a simple alkali / alkaline earth hydride when hydrogen is released in a first step. The dehydrogenation of this simple hydride then occurs as a separate second step. Usually the enthalpies are such that only the first step is considered useful for hydrogen storage. For $\text{Be}(\text{BH}_4)_2$ these two steps correspond to the reverse reactions of Eqs. (5) and (4). The calculated reaction enthalpies of Eqs. (4) and (5) are -0.27 and -0.43 eV/H_2 without ZPEs, and -0.09 and -0.13 eV/H_2 with ZPE corrections, respectively.

Note that per H_2 $\text{Be}(\text{BH}_4)_2$ is slightly more stable than BeH_2 . This would indicate that a one-step reaction directly from the elements, Eq. (3), is more favorable than the two-step reaction via the simple hydride, Eqs. (4) and (5). The enthalpy difference however is very small. In addition kinetic barriers may influence the relative importance of the two reaction paths.

We will now focus on finite temperature properties. For the solids we calculate the Gibbs free energy $G(T)$ in the harmonic approximation

$$G(T) = E^{\text{tot}} + H^{\text{vib}}(T) - TS^{\text{vib}}(T) \quad (6)$$

with

$$H^{\text{vib}}(T) = \int_0^\infty d\omega g(\omega) \left\{ \frac{1}{2}\hbar\omega + \hbar\omega n(\omega) \right\} \quad (7)$$

and

$$S^{\text{vib}}(T) = k_B \int_0^\infty d\omega g(\omega) \{ \beta\hbar\omega n(\omega) - \ln [1 - e^{-\beta\hbar\omega}] \} \quad (8)$$

where $g(\omega)$ is the phonon density of states, $n(\omega) = [\exp(\beta\hbar\omega) - 1]^{-1}$ is the Bose-Einstein occupation number and $\beta = 1/k_B T$. The first term in the integral of Eq. (7) gives the ZPVE and the second term gives the finite temperature contribution. Note that we neglect the PV term (i.e. the distinction between energy and enthalpy), which is a good approximation for solids.

For the Gibbs free energy, the enthalpy and the entropy of the hydrogen gas, we use the values given in

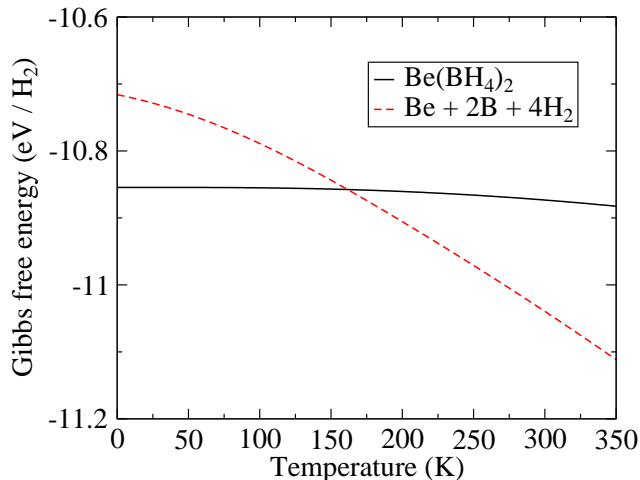


FIG. 7: (color online) Gibbs free energy of $\text{Be}(\text{BH}_4)_2$ and the constituting elements.

Ref. 46. Fig. 7 gives the free energies of $\text{Be}(\text{BH}_4)_2$ and the products of the dehydrogenation reaction, i.e. the left and right hand sides of Eq. (3), at the standard pressure of 1 bar. At 162 K the free energy of the products drops below that of the hydride phase. This intersection of the two free energy curves defines the decomposition temperature.

The predicted desorption temperature and equilibrium pressures rely only on the thermodynamics of the reaction. From the fact that experimentally $\text{Be}(\text{BH}_4)_2$ seems to be stable at room temperature one may conclude that kinetic barriers play an important role in stabilizing $\text{Be}(\text{BH}_4)_2$. In this respect $\text{Be}(\text{BH}_4)_2$ is similar to other boranates and alanates, where decomposition temperatures are much higher than what is expected on the basis of thermodynamics and catalysts have to be applied in order to overcome kinetic barriers.

VI. CONCLUSIONS

We use DFT electronic structure calculations at the GGA level to study the crystal structure, electronic structure and thermodynamics of $\text{Be}(\text{BH}_4)_2$. We optimize the atomic positions and lattice parameters of all compounds involved in possible formation and dehydrogenation reactions. Both the crystal structure and the electronic structure indicate that the bonding between B and H atoms is covalent, and that the bonding between Be and H has

covalent as well as ionic contributions. The crystal structure and the electronic density of states give evidence for $[\text{-BH}_4\text{-Be-}]_n$ (helical) polymers.

The enthalpies of possible formation reactions are calculated including zero point energy corrections. The latter are obtained by the calculating the phonon frequencies of all compounds involved in the reactions. Since not only hydrogen, but also boron and beryllium are relatively light elements, the zero points energies are relatively large for these compounds. The enthalpy of formation of $\text{Be}(\text{BH}_4)_2$ from the elements is -0.39 eV/H_2 without and -0.12 eV/H_2 with zero point energy contributions.

$\text{Be}(\text{BH}_4)_2$ differs from other boranates and alanates in that its dehydrogenation to the elements is thermodynamically slightly more favorable than dehydrogenation via the simple hydride BeH_2 . In alkali or alkaline earth boranates and alanates dehydrogenation always occurs via the alkali or alkaline earth simple hydride. The different behavior of $\text{Be}(\text{BH}_4)_2$ is mainly caused by the high stability of bulk beryllium metal.

$\text{Be}(\text{BH}_4)_2$ follows the general trends in the formation energies that have been observed in alkali and alkaline earth alanates and boranates. Boranates are more stable than the corresponding alanates, lighter cations give compounds that are more unstable, and alkaline earth compounds are more unstable than alkali compounds.⁴⁴ Indeed $\text{Be}(\text{BH}_4)_2$ is less stable than LiBH_4 or $\text{Mg}(\text{BH}_4)_2$. We have not found mentioning of beryllium alanate in the literature, which might indicate that this compound would be too unstable.

Using the calculated phonon spectrum we have calculated free energies within the harmonic approximation to assess thermodynamic properties at finite temperature. We obtain a decomposition temperature of 162 K at a 1 bar pressure.

Acknowledgments

The authors wish to thank Prof. Dr. R.A. de Groot for helpful discussions and J.J. Attema for the use of his imaging software. This work is part of the research programs of ‘Advanced Chemical Technologies for Sustainability (ACTS)’ and the ‘Stichting voor Fundamenteel Onderzoek der Materie (FOM)’, both financially supported by the ‘Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO)’.

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